



## Solubility and cation exchange properties of zeoponic substrates

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### Abstract

A zeoponic plant growth system is defined as the cultivation of plants in artificial soils, which have zeolites as a major component. Batch-equilibrium studies of zeoponic substrates indicate that the nutrients  $\text{NH}_4\text{-N}$  ( $19.7\text{--}73.6\text{ mg dm}^{-3}$ ), P ( $0.57\text{--}14.99\text{ mg dm}^{-3}$ ), K ( $14.8\text{--}104.9\text{ mg dm}^{-3}$ ), and Mg ( $0.11\text{--}6.68\text{ mg dm}^{-3}$ ) are available to plants at sufficient levels. Solution Ca concentrations ( $0.47\text{--}3.40\text{ mg dm}^{-3}$ ) are less than optimal. Solution concentrations of  $\text{NH}_4^+$ ,  $\text{K}^+$ ,  $\text{Ca}^{2+}$ , and  $\text{Mg}^{2+}$  all decreased with increasing clinoptilolite to hydroxyapatite ratio in the sample. Solution concentrations of phosphorus initially increased, reached a maximum value and then decreased with increasing clinoptilolite to hydroxyapatite ratio in the sample. The  $\text{NH}_4^+$ -exchanged clinoptilolite is more efficient in dissolving synthetic hydroxyapatite than the  $\text{K}^+$ -exchanged clinoptilolite. The addition of calcite, dolomite or wollastonite to the zeoponic substrate resulted in an exponential decrease in solution P concentrations (from  $15.05$  to  $1.49\text{ mg dm}^{-3}$ ). The exponential rate of decay was greatest for calcite ( $5.60\text{ wt.}\%^{-1}$ ), intermediate for wollastonite ( $2.85\text{ wt.}\%^{-1}$ ) and least for dolomite ( $1.58\text{ wt.}\%^{-1}$ ). Additions of the three minerals resulted in linear increases in the solution Ca concentrations (from  $0.51$  to  $2.47\text{ mg dm}^{-3}$ ). The rate of increase was greatest for calcite ( $3.64\text{ mg dm}^{-3}\text{ wt.}\%^{-1}$ ), intermediate for wollastonite ( $2.41\text{ mg dm}^{-3}\text{ wt.}\%^{-1}$ ) and least for dolomite ( $0.61\text{ mg dm}^{-3}\text{ wt.}\%^{-1}$ ). The observed changes in solution P and Ca concentrations are consistent with the solubilities of calcite, dolomite and wollastonite and with expected changes due to a common ion effect with Ca.

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### 1. Introduction

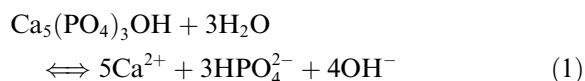
An artificial plant growth substrate composed of zeolite and phosphate minerals (i.e. zeoponic

substrate) can serve as a controllable and renewable fertilization system to provide plant growth nutrients [1–4]. Moreover, the slow release nature of zeoponic substrates can mitigate the adverse effects of ground- and surface-water contamination due to leaching of highly soluble and concentrated fertilizers. Zeoponic substrates have been developed at the National Aeronautics and Space Administration (NASA) as plant growth

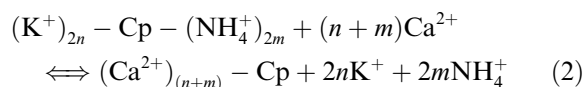
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substrates for use in bioregenerative life-support systems required for future long-duration space missions (e.g., Mars transit vehicles, planetary outposts). These zeoponic systems slowly release some [5] or all of the essential plant growth nutrients [6]. The primary components are  $\text{NH}_4^+$ - and  $\text{K}^+$ -exchanged clinoptilolite-rich tuff (Cp, chosen due to its high selectivity for  $\text{NH}_4^+$  and  $\text{K}^+$ ) and either natural or synthetic hydroxyapatite (Ap). Other minerals, such as dolomite (Dol), are added to buffer pH or provide an additional source of Ca. The concept behind the zeoponic system is that the low solubility exhibited by Ap will be overcome by the sequestering of  $\text{Ca}^{2+}$  by the Cp via ion exchange. Specifically the chemical equilibria among Cp, Ap, and water will be dominated by the dissolution of Ap, which releases  $\text{Ca}^{2+}$  into solution, and subsequent ion exchange between  $\text{Ca}^{2+}$  and  $\text{K}^+$  or  $\text{NH}_4^+$  on extra-framework sites in the Cp. These reactions can be represented as:



and



where Cp = clinoptilolite. Reaction one represents a simplified dissolution of Ap ignoring the trace micronutrients present [5]. Reaction (2) represents the exchange of  $\text{Ca}^{2+}$  (which has dissolved into solution from Ap) by Cp that results in the shifting of both reactions to the right. The goals of the present study are to, by means of a series of batch-equilibration experiments, determine: (1) the solution concentrations of the macro-nutrients  $\text{NH}_4$ -N, P, K, Ca, and Mg in synthetic Ap and Cp mixtures, (2) the solution concentration effects of varying the Cp to synthetic Ap ratio in these mixtures, (3) the solution concentration effects of varying the fraction of  $\text{K}^+$  vs.  $\text{NH}_4^+$  on extra-framework sites of the Cp in these mixtures and (4) to determine if  $\text{Ca}^{2+}$  can be increased in solution by adding a second Ca-bearing mineral: calcite (Cal), Dol, or wollastonite (Wol) to the zeoponic substrate. These are the first ever batch-equilibrium experiments on zeoponic substrates that

include synthetic nutrient substituted Ap and the first ever experiments addressing the addition of a second Ca-bearing mineral.

### 1.1. Previous work

Zeoponic systems have been successfully demonstrated in Cuba and Bulgaria, but these systems require periodic treatments with fertilizers or nutrient solutions [7]. Moller and Mogensen [8] demonstrated an increase in soil solution P concentrations due to enhanced phosphate dissolution by the addition of Na-saturated synthetic zeolite. Lai and Eberl [9] combined 1 g of  $\text{NH}_4^+$ -exchanged Cp rich tuff (from Barstow, California) with 200 mg of phosphate rock (mainly carbonate apatite, from Florida) in 50 ml distilled  $\text{H}_2\text{O}$ . Chesworth et al. [10] combined 1 g apatite with 1 g unexchanged Cp (from Ash Meadows, California) in 100 ml distilled  $\text{H}_2\text{O}$ . Barbarick et al. [11] combined  $\text{NH}_4^+$ -exchanged Cp (from the Washakie Basin in Wyoming [12]) and North Carolina Phosphate Rock (NCPR) with Cp to NCPR ratios of 1.5, 3, 4.5, 6, and 7 utilizing a 2 ml  $\text{g}^{-1}$  deionized water to soil ratio. Allen et al. [5] performed experiments utilizing  $\text{K}^+$ -exchanged Cp (from San Miguel, Texas) and NCPR with Cp to NCPR ratios of 1, 2, 3, 5, 10, and 20 utilizing deionized water to soil ratios ranging from 20 to 38.1 ml  $\text{g}^{-1}$ . Lai and Eberl [9], Chesworth et al. [10], and Barbarick et al. [11] reported an increase in P released from phosphate rock by the addition of Cp. Allen et al. [5] concluded that the mixing of  $\text{NH}_4^+$ - and  $\text{K}^+$ -exchanged Cp with phosphate rock, increased the solubility of the phosphate rock and resulted in the simultaneous release of  $\text{NH}_4^+$  and  $\text{K}^+$  into solution. These mixtures provide enough N, P, and K in solution to support plant growth. Calcium in solution was lower than optimal for plant growth due to the removal of  $\text{Ca}^{2+}$  from solution by exchange onto extra-framework sites in the Cp.

Plant growth experiments on dwarf wheat (*Triticum aestivum* L. cv. 'Super Dwarf') grown in the zeoponic substrate used in the present study indicate a positive correlation between the percent of zeoponic material in the substrate and dry-matter production [13], however the dry-matter production was less than that in controls. Poor seed

production has been noted in the wheat grown in zeoponic substrate. Goins et al. [14] noted that dwarf wheat (*Triticum aestivum* L. cv. 'USU-Super Dwarf') grown in zeoponic substrates ( $K^+$ -exchanged and  $NH_4^+$ -exchanged Cp and synthetic Ap produced excessive seedless tillers compared to wheat produced by fertilization via a nutrient solution. Gruener et al. [13] also reported poor seed production and suggested that the low yield may have been attributed to high  $NH_4^+$  in solution causing  $NH_4^+$ -induced Ca deficiency and/or high P concentrations, which may have inhibited the uptake of other essential plant nutrients. A  $NH_4^+$ -induced Ca deficiency was also proposed by Steinberg et al. [15] to explain excess seedless tillers of wheat (*Triticum aestivum* L. cv. 'USU-Apogee') grown in a zeoponic substrate (2:2:1:0.55 mixture (by weight) of  $K^+$ -exchanged Cp,  $NH_4^+$ -exchanged Cp coated with ferrihydrite, synthetic Ap, Dol) compared to wheat grown in a recirculating hydroponic system. Henderson et al. [16] successfully increased wheat (*Triticum aestivum* L. cv. 'USU-Apogee') dry matter and seed production, in zeoponic plant growth experiments by adding nitrifying bacteria (to convert  $NH_4-N$  to  $NO_3-N$ ), Dol (to lower apatite dissolution) and ferrihydrite (to sequester P). However, even with increased yields, plant tissue concentrations of Ca ranged from 0.13 to 0.2 wt.% (day 30 samples) which were lower than the expected levels of 0.2 to 0.55 wt.% reported in field-grown wheat [17]. Batch equilibrium solution studies of the same zeoponic substrates used in the above-mentioned plant growth experiments [18] indicated that K, N, P and Mg are present in solution at plant-sufficient levels, however Ca may be deficient. In this case the low  $Ca^{2+}$  in solution was attributed to the high degree of  $Ca^{2+}$  exchanged onto extra-framework sites in the Cp.

The positive plant growth results reported by Henderson et al. [16] due to addition of Dol to the zeoponic substrate led us to propose the hypothesis that another Ca-bearing mineral with higher solubility than Dol, and containing no harmful ions, such as Cal or Wol could be used to increase the bioavailability of  $Ca^{2+}$  in zeoponic substrates. The published solubility products for Cal, Dol, and Wol are listed in Table 1. Because Cal, Dol

Table 1

Published solubility products for apatite, calcite, dolomite and wollastonite

Mineral	Solubility product ( $-\log K_{sp}$ , 25 °C)	Reference
Apatite	58.3	[19]
Apatite (synthetic)	$58 \pm 1$	[20]
Apatite (natural)	70	[20]
Hydroxyapatite	44.2	[21]
Calcite	8.35	[22]
Calcite	8.33–8.48	[23]
Calcite	8.48	[21]
Dolomite	$17.2 \pm 0.2$	[24]
Dolomite	16.7	[25]
Dolomite (ordered)	17.09	[26]
Dolomite (disordered)	16.54	[26]
Dolomite	17.0	[21]
Wollastonite	12.996	[21]

and Wol are all much more soluble than Ap, the addition of one of them to the Ap plus Cp mixture should result in higher concentrations of  $Ca^{2+}$  in solution. Additionally, the dissolution of Ap should be inhibited because its solubility is diminished by the presence of one of its own ions in solution (i.e.  $Ca^{2+}$ ) from the added Ca-bearing mineral by what is called the common-ion effect (e.g. [27]). The addition of Cal ( $CaCO_3$ ) and Wol ( $CaSiO_3$ ) should increase the concentration of  $Ca^{2+}$  in solution and should also lower the amount of P in solution due to the common ion effect on Ap dissolution. The addition of Dol ( $CaMg(CO_3)_2$ ) should increase the concentrations of  $Ca^{2+}$  and  $Mg^{2+}$  in solution. The net change in the dissolution of Ap due to the addition of Dol will be a sum of the off-setting effects of Ca's common-ion effect and Mg's propensity to increase the solubility of the Ap. The increased concentration of  $Ca^{2+}$  (and  $Mg^{2+}$  for Dol) in solution may result in increased cation exchange in the Cp resulting in increased  $K^+$  or  $NH_4^+$  in solution.

## 2. Experimental

### 2.1. Materials

The starting materials consist of Cp mined from the Fort LeClede deposit of the Green River

Formation in Sweetwater County, Wyoming [28], a synthetic Ap developed at NASA's Johnson Space Center Advanced Life Support Laboratory [29], Cal from Montana (D. J. Minerals M-61), Dol (Baker Grandol Regular # 4) and Wol from the NYCO Minerals Inc. Lewis mine, northeastern Adirondacks, New York [30,31]. All materials were sieved and the 0.5 to 1.0 mm sieve fraction was used.

X-ray diffraction analysis of the Cp indicate that it is relatively pure clinoptilolite [32] containing, on average, greater than 95% clinoptilolite, less than 5% quartz and trace amounts of smectite. The composition of the natural Cp is shown in Table 2 [32]. Based on a 72 oxygen per formula unit the Cp has the formula  $(\text{Na}_{3.55} \text{K}_{0.87} \text{Ca}_{0.63} \text{Mg}_{0.11} \text{Fe}_{0.03} \text{Ti}_{0.01} \text{Al}_{0.21}) \text{Al}_{6.66} \text{Si}_{29.34} \text{O}_{72} \cdot 24\text{H}_2\text{O}$ . The framework Si to Al ratio is 4.41 which is greater than the clinoptilolite/heulandite boundary of 4.0 [33,34]. Sodium is the dominant extra-framework cation with subsidiary amounts of K and Ca and trace amounts of Mg, Fe, and Ti. The Cp has a cation exchange capacity of 199 cmol of charge per kg

Table 2  
Composition of clinoptilolite (Cp) and hydroxyapatite (Ap) used in experiments

Cp		Ap	
Oxide	wt.%	Oxide	wt.%
SiO <sub>2</sub>	70.36	CaO	46.8
Al <sub>2</sub> O <sub>3</sub>	13.99	P <sub>2</sub> O <sub>5</sub>	39.61
Na <sub>2</sub> O	4.39	Fe <sub>2</sub> O <sub>3</sub>	1.21
K <sub>2</sub> O	1.64	MgO	2.25
CaO	1.42	SiO <sub>2</sub>	0.59
MgO	0.18	SO <sub>3</sub>	2.07
FeO	0.1	OH	3.61
MnO	0.01		
TiO <sub>2</sub>	0.02		
Cr <sub>2</sub> O <sub>3</sub>	0.01		
P <sub>2</sub> O <sub>5</sub>	0.01		
SO <sub>2</sub>	0.02		
Element	μg mg <sup>-1</sup>	Element	μg mg <sup>-1</sup>
Ni	<18.5	Na	23.74
Co	0.8	K	18.26
Sr	421	Mn	330
Cs	2	Cu	28.9
Rb	81.6	Zn	282
Zr	206.3	Sr	140
Ba	906		
As	1.6		

Table 3  
Mean composition of Wol, Cal and Dol used in experiments

	Wol	Cal	Dol
	<i>n</i> = 25	<i>n</i> = 28	<i>n</i> = 25
MgO (wt.%)	0.00 (0.00)	0.00 (0.00)	17.66 (0.12)
Al <sub>2</sub> O <sub>3</sub> (wt.%)	0.03 (0.02)		
SiO <sub>2</sub> (wt.%)	51.23 (0.14)		
CaO (wt.%)	48.37 (0.19)	55.72 (0.05)	35.03 (0.15)
MnO (wt.%)	0.19 (0.03)	0.25 (0.04)	0.02 (0.03)
FeO (wt.%)	0.49 (0.07)	0.09 (0.03)	0.31 (0.08)
CO <sub>2</sub> (wt.%)		43.94 (0.01)	46.98 (0.02)
Total (wt.%)	100.32 (0.23)	100.00 (0.00)	100.00 (0.00)
<i>Moles per 6 oxygen</i>			
Mg	0.00 (0.00)	0.00 (0.00)	0.82 (0.01)
Al	0.00 (0.00)		
Si	1.98 (0.00)		
Ca	2.01 (0.01)	1.99 (0.00)	1.17 (0.01)
Mn	0.01 (0.00)	0.01 (0.00)	0.00 (0.00)
Fe	0.02 (0.00)	0.00 (0.00)	0.01 (0.00)
C		2.00 (0.00)	2.00 (0.00)

Numbers in parentheses represent one standard deviation (*n* = # of analyses).

[13] determined by a CsCl method described by Ming and Dixon [35]. The Cp was exchanged into K<sup>+</sup>-exchanged Cp and NH<sub>4</sub><sup>+</sup>-exchanged Cp using the method of Allen et al. [5]. The nutrient substituted synthetic Ap, (Table 2) was synthesized using the method of Golden and Ming [29]. In addition to the major components Ca and P it contains Mg, S and the plant essential micronutrients (Cu, Fe, K, Mn, Na, Si, Sr, and Zn) incorporated into the synthetic Ap structure. The compositions of Cal, Dol and Wol (Table 3) were determined using a Cameca SX100 Electron Probe Micro Analyzer (EPMA) operated at 15 kV and a beam current of 10 nanoamps using well-characterized silicate and carbonate standards. The Cal is close to pure, containing trace amounts of Fe and Mn. The Dol is non-stoichiometric, having the formula  $\text{Ca}_{1.17}\text{Mg}_{0.82}(\text{CO}_3)_2$ . The Wol is stoichiometric and pure, containing trace amounts of Fe and Mn, which is common [36].

## 2.2. Experimental methods

### 2.2.1. Sample assembly

Two series of batch-equilibration experiments were performed. One series combined varying

amounts of  $K^+$ -exchanged Cp,  $NH_4^+$ -exchanged Cp, and synthetic Ap. Cp to synthetic Ap weight ratios of 1, 2, 4, 8, 16, and 32 were studied for ratios of  $K^+$  to  $NH_4^+$  and  $K^+$  on Cp extra-framework sites ( $E_K$ ) of 1, 0.5, and 0. The 0.5  $E_K$  value was achieved by combining equal weights of  $K^+$ -exchanged Cp and  $NH_4^+$ -exchanged Cp. For example, a sample with a Cp/Ap ratio of 4:1 and an  $E_K$  of 0.5 consisted of 1.000 g of  $K^+$ -exchanged Cp, 1.000 g of  $NH_4^+$ -exchanged Cp, and 0.500 g of synthetic Ap.

In the second series, varying amounts of Cal, Dol or Wol were combined with  $K^+$ -exchanged Cp,  $NH_4^+$ -exchanged Cp and Ap. The Ap in this series of experiments was heated in a kiln at 400 °C prior to grinding and sieving. The Cp to Ap ratio was held constant at 4:1. The mass ratio of  $K^+$ -exchanged to  $NH_4^+$ -exchanged Cp was held constant at 1:1. The amount of the third mineral (Cal, Dol or Wol) was varied at 0, 5, 10, 15, 20, 25 and 50 wt.%. For example, a sample with 20 wt.% Cal consisted of 0.500 g of Cal, 0.000 g of Dol, 0.000 g of Wol, 0.800 g of  $K^+$ -exchanged Cp, 0.800 g of  $NH_4^+$ -exchanged Cp and 0.400 g of Ap. Each treatment was replicated three times.

In every case the total solid mass of 2.5 g was combined with 100 ml of de-ionized water in a 125 ml Erlenmeyer flask, resulting in a constant fluid–solid ratio of 40 ml g<sup>-1</sup>. Each flask was capped with a foam stopper to obtain free exchange with atmospheric CO<sub>2</sub> and was placed on an orbital shaker set at 90 rpm and 25 °C. This experimental procedure differs from Allen et al. [5] in that they placed mixtures containing 0.25 g of  $K^+$ -exchanged Cp and varying amounts of phosphate rock (to give the desired Cp/phosphate rock mass ratio) in stoppered centrifuge tubes containing 10 ml of deionized water. This resulted in different fluid to solid ratios (ranging from 20 to 38.1 ml g<sup>-1</sup>) for each Cp to phosphate rock ratio studied. In the present study, the fluid to solid ratio was held constant for each treatment. The fluid to solid ratio was also held constant in the experiments performed by Lai and Eberl (41.7 ml g<sup>-1</sup> [9]), Chesworth et al. (50 ml g<sup>-1</sup> [10]) and Barbarick et al. (2 ml g<sup>-1</sup> [11]).

### 2.2.2. Equilibration time

The shaking time required for a mixture of Cp and Ap to approach a steady state has been studied by Allen et al. [5] and Beiersdorfer [37]. Allen et al. [5] recommended a shaking time of 96 h based on measurement of solution K concentrations in mixtures of 0.25 g of Cp, 0.05 g of naturally occurring phosphate rock, and 10 ml of water in a stoppered centrifuge tube. Solution K concentrations increased rapidly for the first 16 h of shaking followed by slight increases for up to 96 h. There was little increase in K concentration between 72 and 96 h. Beiersdorfer [37] measured concentrations of P and K as a function of shaking time in zeoponic substrates consisting of 2 g of  $K^+$ -exchanged Cp, 0.5 g of synthetic Ap, and 100 ml of de-ionized water in a 125 ml Erlenmeyer flask. Phosphorus and K concentrations increased rapidly over the first 210 h and reached “steady state” concentrations after 400 h of shaking time. Without explaining their selections, Lai and Eberl [9] and Barbarick et al. [11] selected 48 h and Chesworth et al. [10] chose 70 h for equilibration experiments containing zeolite and phosphate rock. Woods and Gunter [38] found no change in solution concentration in Na<sup>+</sup>- and Cs<sup>+</sup>-exchanged Cp-rich rock after 24 h. Palmer and Gunter [39] found that near steady-state conditions were reached after 240 h in Sr<sup>2+</sup>-exchanged Cp. In order to be confident that mixing time was adequate for achieving a steady state in solution concentrations, samples in the present study were removed at 500 h.

### 2.2.3. Analysis of solutions

The supernatant solutions were filtered through a #42 Whatman filter (nominal (98% retention) pore size rating of 2.5 µm). Potassium, magnesium, and calcium concentrations in solution were determined by flame atomic absorption spectroscopy. Phosphorus was determined using an ascorbic-acid, molybdophosphate-blue colorimetric method [40]. Ammonium and pH were measured using ion selective electrodes. Ionic strength was calculated from measured electrical conductivity using the empirical relationship of Griffin and Jurinak [41] where:

Ionic strength ( $\text{mol dm}^{-3}$ ) = 0.0127 electrical conductivity ( $\text{dS m}^{-1}$ ). Least squares regression of data was performed using the software program DeltaGraph Pro version 3.0 (SPSS Inc. Chicago, IL). Equilibrium estimates of Ap dissolution over the observed range of pH were performed using the chemical speciation program Visual MINTEQ [42], a Windows version of MINTEQA2 ver 4.0 [21].

### 3. Results

#### 3.1. Variation in Ap/Cp and $E_K$

Solution pH, ionic strength, and phosphorus, ammonium, potassium, magnesium, and calcium concentrations after 500 h of shaking time for samples containing various Cp to synthetic Ap ratios, as well as varying  $E_K$  are shown in Table 4. Ammonium was not analyzed in samples that contained no  $\text{NH}_4^+$ -exchanged Cp (i.e. samples with  $E_K$  of 1). Potassium however, was measured at very low levels in solution in samples that con-

tain only  $\text{NH}_4^+$ -exchanged Cp (i.e. samples with  $E_K$  of 0). The presence of  $\text{K}^+$  in solution is most likely due to the incomplete exchange of  $\text{NH}_4^+$  for naturally occurring  $\text{K}^+$  during the  $\text{NH}_4^+$ -exchange procedure due to the higher selectivity for  $\text{K}^+$  on Cp extra-framework sites.

#### 3.1.1. Phosphorus

Solution P concentrations as a function of Cp/Ap ratio and  $E_K$  are shown in Fig. 1. For a given Cp/Ap ratio, P concentrations are greater for samples with a lower  $E_K$ . This relationship reflects the higher selectivity for  $\text{K}^+$  relative to  $\text{NH}_4^+$  by Cp on extra-framework sites as noted by Ames [43]. In other words, it is “easier” for  $\text{Ca}^{2+}$  to replace  $\text{NH}_4^+$  on extra-framework sites in the Cp than it is for  $\text{Ca}^{2+}$  to replace  $\text{K}^+$ . This increased facility to exchange extra-framework  $\text{NH}_4^+$  with  $\text{Ca}^{2+}$  results in greater synthetic Ap dissolution and higher P concentrations with decreasing  $E_K$ . A similar trend was observed by Allen et al. [5]. For a given  $E_K$  (1, 0.5 or 0), P concentrations initially increased with increasing Cp/Ap ratio until the solution P reached a max-

Table 4

Solution pH, ionic strength (IS), and concentrations of phosphorus, potassium, ammonium, magnesium and calcium as a function of Cp/Ap ratio and  $E_K$

Cp/ Ap	$E_K$	pH	IS ( $\text{mmol dm}^{-3}$ )	P ( $\text{mg dm}^{-3}$ )	$\text{NH}_4$ ( $\text{mg dm}^{-3}$ )	K ( $\text{mg dm}^{-3}$ )	Mg ( $\text{mg dm}^{-3}$ )	Ca ( $\text{mg dm}^{-3}$ )
0	n.a.	7.70 (0.11)	4.03 (0.20)	0.26 (0.12)	n.a.	n.a.	36.21 (2.43)	19.73 (0.32)
1	1	7.87 (0.20)	3.78 (0.06)	0.57 (0.03)	n.a.	104.85 (0.73)	6.68 (0.33)	3.40 (0.09)
2	1	7.90 (0.02)	3.46 (0.33)	0.98 (0.01)	n.a.	98.75 (1.54)	3.01 (0.13)	1.88 (0.04)
4	1	7.89 (0.06)	2.80 (0.08)	1.77 (0.03)	n.a.	86.59 (1.78)	1.38 (0.11)	1.10 (0.12)
8	1	7.94 (0.05)	2.35 (0.17)	3.10 (0.24)	n.a.	70.43 (3.15)	0.58 (0.16)	0.79 (0.05)
16	1	7.87 (0.15)	1.87 (0.08)	4.06 (0.41)	n.a.	58.93 (4.72)	0.28 (0.06)	0.88 (0.44)
32	1	7.88 (0.10)	1.49 (0.03)	4.59 (0.68)	n.a.	47.60 (2.16)	0.14 (0.01)	0.49 (0.03)
1	0.5	8.22 (0.01)	5.07 (0.03)	1.00 (0.05)	45.17 (0.31)	33.48 (0.46)	5.26 (0.26)	3.07 (0.31)
2	0.5	8.29 (0.01)	4.45 (0.03)	2.01 (0.08)	43.16 (0.10)	30.35 (0.34)	2.26 (0.10)	2.05 (0.33)
4	0.5	8.31 (0.01)	3.80 (0.03)	4.50 (0.28)	39.21 (0.48)	27.24 (0.52)	1.05 (0.03)	1.20 (0.13)
8	0.5	8.20 (0.02)	3.01 (0.16)	6.94 (0.79)	32.16 (1.75)	21.93 (1.01)	0.44 (0.07)	1.06 (0.21)
16	0.5	8.09 (0.05)	2.41 (0.11)	8.53 (0.68)	26.01 (1.42)	17.59 (0.68)	0.21 (0.03)	0.80 (0.15)
32	0.5	8.03 (0.03)	1.85 (0.09)	7.91 (0.30)	19.73 (1.07)	14.83 (0.64)	0.12 (0.02)	0.90 (0.19)
1	0	8.35 (0.01)	5.69 (0.04)	2.43 (0.15)	73.64 (0.51)	1.21 (0.02)	2.48 (0.02)	2.12 (0.01)
2	0	8.39 (0.02)	4.95 (0.08)	4.95 (0.10)	68.06 (0.57)	1.06 (0.09)	1.02 (0.04)	1.23 (0.39)
4	0	8.36 (0.02)	4.20 (0.15)	9.39 (0.50)	59.11 (2.39)	0.94 (0.07)	0.44 (0.05)	0.92 (0.11)
8	0	8.28 (0.02)	3.66 (0.12)	14.19 (1.17)	51.57 (1.46)	0.82 (0.08)	0.22 (0.02)	0.47 (0.05)
16	0	8.15 (0.01)	2.73 (0.07)	12.83 (0.62)	37.88 (1.09)	0.68 (0.03)	0.11 (0.01)	0.62 (0.17)
32	0	7.94 (0.02)	1.92 (0.06)	11.02 (0.90)	26.32 (1.23)	0.63 (0.23)	0.17 (0.17)	0.84 (0.60)

Values represent average of three replicates. Numbers in parentheses represent one standard deviation. n.a. = not analyzed.

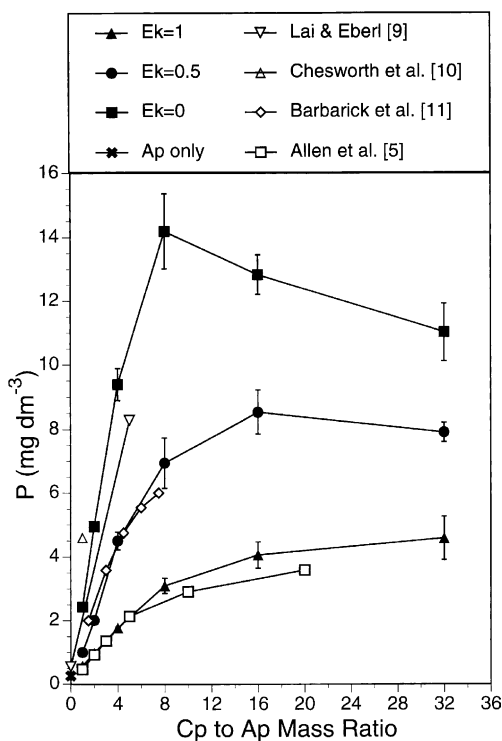


Fig. 1. Solution phosphorus concentration as a function of Cp to Ap mass ratio and  $E_K$ . Solid symbols represent the average of three replicates. Error bars represent  $\pm 1\sigma$ . Data from Lai and Eberl [9], Chesworth et al. [10] and Barbarick et al. [11] have  $E_K = 0$ . Data from Allen et al. [5] have  $E_K = 1$ . Lines connecting data points are added to show trends only and do not imply curve fitting.

imum value and then decreased with increasing Cp/Ap ratio.

Phosphorus concentrations reported by Lai and Eberl [9], Chesworth et al. [10], Barbarick et al. [11] and Allen et al. [5] are shown in Fig. 1 for comparison with P concentrations in solutions contacted with varying amounts of Cp and synthetic Ap. Data from these four studies using naturally occurring phosphate rock are, for the most part, comparable with the data reported here for nutrient substituted synthetic Ap. The reported solution P concentrations from Barbarick et al. [11] utilizing  $\text{NH}_4^+$ -exchanged Cp are identical to the  $E_K = 0.5$  data reported here but are lower than the  $\text{NH}_4^+$ -exchanged Cp data ( $E_K = 0$ ). The only significant difference between the Allen et al. [5] data and the present study occur at higher Cp/Ap

ratio where the P concentrations reported by Allen et al. [5] (for Cp/Ap ratios of 10 and 20) are lower than comparable concentrations from the present study (for Cp/Ap ratios of 8, 16, and 32).

The results of the present study reinforce the effect of Cp/Ap ratio on P concentrations previously described by Lai and Eberl [9], Chesworth et al. [10], Barbarick et al. [11], and Allen et al. [5]. Minor differences between the data may be attributable to the different materials used in each study and/or the different fluid to solid ratios. The trend observed in the present study of decreasing P concentrations at higher Cp/Ap ratio was not observed in the data from Barbarick et al. [11] and Allen et al. [5] because their experiments did not include treatments in the Cp/Ap ratio region where the trend is most apparent (i.e. higher Cp/Ap ratio data). Barbarick et al. [11] fit a linear relationship between P concentrations and Cp/Ap ratio:

$$[P] = (\text{Cp/Ap ratio}) + 0.74 \text{ [11]}.$$

However, the data from both Barbarick et al. [11] and Allen et al. [5] do show a decrease in slope (i.e.  $\Delta[P]/\Delta(\text{Cp/Ap})$ ) at their highest Cp/Ap ratio, consistent with the trend observed in the present study. However, the low water to soil ratio (2  $\text{ml g}^{-1}$ ) used by Barbarick et al. [11] may make any comparison of the present study with their data inappropriate.

The trend of decreasing P concentrations at higher Cp/Ap ratio in the present study may be related to the amount of Ap available for dissolution. Fig. 2 shows P concentrations normalized to the minimum amount of Ap for each series of experiments (0.0758 g for the present study, 2.94 g for Barbarick et al. [11], and 0.0125 g for Allen et al. [5]) versus Cp/Ap ratio. The normalized P concentrations all increase linearly with Cp/Ap ratio. As the Cp/Ap ratio increases the number of Cp extra-framework sites per g of synthetic Ap also increases. The increase in Cp extra-framework sites results in an increase in the number of  $\text{Ca}^{2+}$  ions that replace  $\text{NH}_4^+$  or  $\text{K}^+$  per g of synthetic Ap. The increased cation exchange results in increased synthetic Ap dissolution and higher P concentrations per g of synthetic Ap with increasing Cp/Ap ratio. The observed trend in Fig. 2 is consistent with the trend

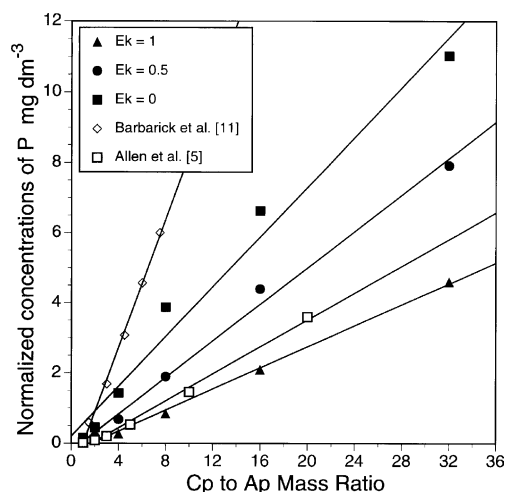


Fig. 2. Normalized solution phosphorus concentration as a function of Cp to Ap mass ratio and  $E_K$ . Solid symbols represent the average of three replicates. Data from Barbarick et al. [11] have  $E_K = 0$ . Data from Allen et al. [5] have  $E_K = 1$ . Lines represent linear fit of data by least squares regression.

in the un-normalized data (Fig. 1). The  $\text{NH}_4^+$ -exchanged Cp of Barbarick et al. [11] is more efficient in dissolving naturally occurring Ap than the  $\text{K}^+$ -exchanged Cp used by Allen et al. [5]. The data from the present study also indicate that  $\text{NH}_4^+$ -exchanged Cp is more efficient in dissolving synthetic Ap than the  $\text{K}^+$ -exchanged Cp, due to the higher selectivity for  $\text{K}^+$  relative to  $\text{NH}_4^+$  by Cp on extra-framework sites, as described above.

General differences in normalized P concentrations between treatments containing naturally occurring Ap and synthetic Ap occur for both  $\text{K}^+$ -exchanged Cp and  $\text{NH}_4^+$ -exchanged Cp and may reflect on the relative solubilities of the naturally occurring Ap and synthetic Ap. The normalized P concentrations for treatments containing naturally occurring Ap and  $\text{K}^+$ -exchanged Cp [5] are greater than those for treatments containing synthetic Ap and  $\text{K}^+$ -exchanged Cp ( $E_K = 1$  from the present study). A comparison of treatments containing  $\text{NH}_4^+$ -exchanged Cp (Barbarick et al. [11] versus  $E_K = 0$  from the present study) indicate the same relationship, suggesting that the naturally occurring Ap is more soluble than the synthetic Ap used in the present study. Phosphorus concentrations from treatments con-

taining Ap only (see Fig. 1) also indicate that naturally occurring Ap is more soluble than the synthetic Ap. Lai and Eberl [9] reported a P concentration of  $0.55 \text{ mg dm}^{-3}$  for a treatment containing phosphate rock only in comparison to a P concentration of  $0.26 \text{ mg dm}^{-3}$  for a treatment from the present study containing synthetic Ap only. However, these general trends are ignoring differences in the CEC of the Cp used in each study (199 for the present study, 140 for Barbarick et al. [11], and 170 for Allen et al. [5] (measured as cmol of charge per kg)) as well as differences in fluid to solid ratios (40 for the present study, 2 for Barbarick et al. [11], and 20 to 38.1 for Allen et al. [5] (measured as  $\text{ml g}^{-1}$ )).

### 3.1.2. Calcium

Solution Ca concentrations as a function of Cp/Ap ratio and  $E_K$  are shown in Fig. 3. Solution Ca concentrations are low (ranging from 0.47 to  $3.40 \text{ mg dm}^{-3}$ ) in mixtures containing Cp compared to Ca in solution of the synthetic Ap only sample ( $19.73 \text{ mg dm}^{-3}$ ). This is due to Ca, which is released by Ap dissolution, being exchanged onto

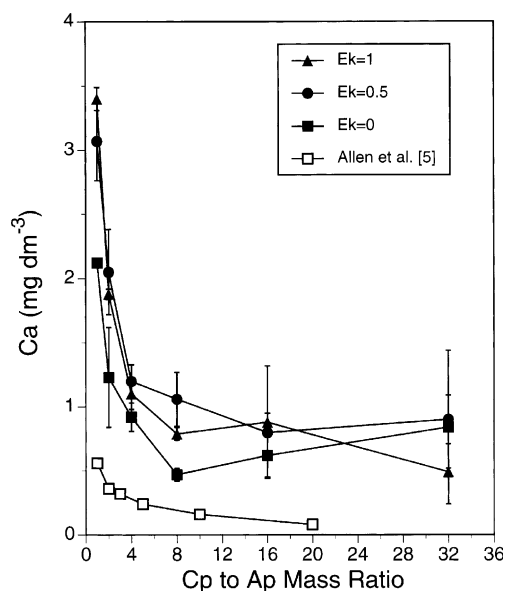


Fig. 3. Solution calcium concentration as a function of Cp to Ap mass ratio and  $E_K$ . Solid symbols represent the average of three replicates. Error bars represent  $\pm 1\sigma$ . Data from Allen et al. [5] have  $E_K = 1$ . Lines connecting data points are added to show trends only and do not imply curve fitting.



extra-framework sites in the Cp. Calcium concentrations decreased with increasing Cp/Ap ratio for lower Cp/Ap ratio values (e.g. 1, 2 or 4) and are relatively constant for Cp/Ap ratio values of 8, 16, and 32. For a Cp/Ap ratio of 1, Ca concentrations increased with greater  $E_K$ . A trend between Ca concentrations and  $E_K$  was not observed in treatments with other Cp/Ap ratios. Calcium concentrations from NCPR samples reported by Allen et al. [5], ranging from 0.1 to 0.6 mg dm<sup>-3</sup> (Fig. 3), show a similar trend and are lower than the Ca concentrations reported here.

The lower solution Ca concentrations in treatments containing the naturally occurring NCPR [5] compared to treatments containing synthetic Ap (the present study) could be attributable to differences in the solubilities of NCPR versus synthetic Ap or to differences in the CEC of the Cp in either treatment. However, the lower solution Ca concentrations in treatments containing the naturally occurring NCPR would be consistent with the NCPR being less soluble than the synthetic Ap, which is opposite the trend observed in the P data. The lower solution Ca concentrations are also inconsistent with an explanation based on differences in the CEC of the Cp. The CEC of the Cp used by Allen et al. [5] is lower than the CEC for the Cp used in the present study.

### 3.1.3. Magnesium

Solution Mg concentrations as a function of Cp/Ap ratio and  $E_K$  are shown in Fig. 4 and are similar in many respects to solution Ca. Measured Mg concentrations are low (ranging from 0.11 to 6.68 mg dm<sup>-3</sup>) compared to the synthetic Ap only sample, which had a solution Mg concentration of 36.21 mg dm<sup>-3</sup>. For a given Cp/Ap ratio, Mg concentrations are greater for samples with a greater  $E_K$ . This relationship is more pronounced at lower Cp/Ap ratio values (e.g. 1, 2, or 4) and does not exist at Cp/Ap ratio values of 16 or 32. Like P, the relationship between Mg concentration and  $E_K$  may be due to the higher ion selectivity for K<sup>+</sup> over NH<sub>4</sub><sup>+</sup> on extra-framework sites of Cp. Magnesium does not compete very well with K<sup>+</sup> on extra-framework sites but does slightly better with NH<sub>4</sub><sup>+</sup>.

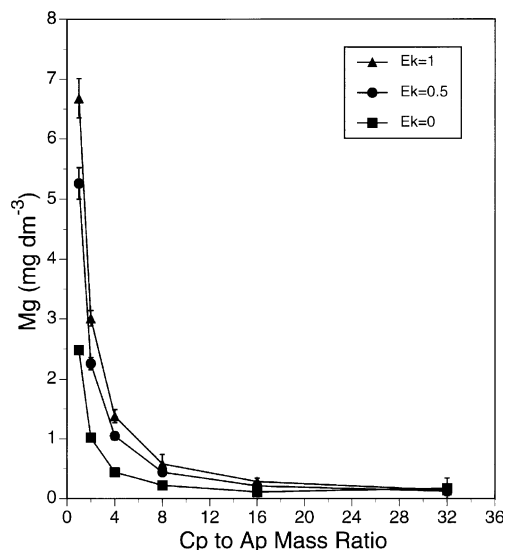


Fig. 4. Solution magnesium concentration as a function of Cp to Ap mass ratio and  $E_K$ . Symbols represent the average of three replicates. Error bars represent  $\pm 1\sigma$ . Lines connecting data points are added to show trends only and do not imply curve fitting.

### 3.1.4. Potassium

Solution K concentrations as a function of Cp/Ap ratio and  $E_K$  are shown in Fig. 5. For both an

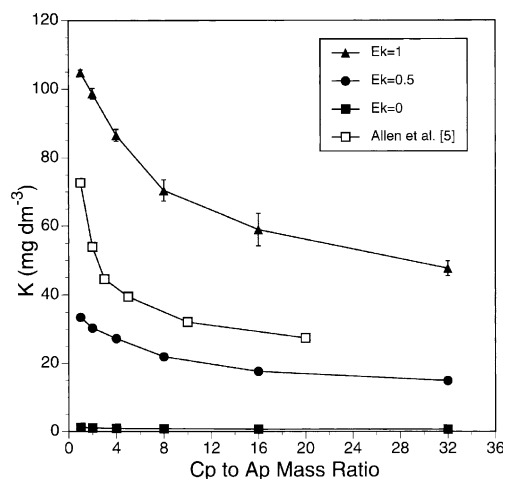


Fig. 5. Solution potassium concentration as a function of Cp to Ap mass ratio and  $E_K$ . Solid symbols represent the average of three replicates. Error bars represent  $\pm 1\sigma$ . Data from Allen et al. [5] have  $E_K = 1$ . Lines connecting data points are added to show trends only and do not imply curve fitting.

$E_K$  of 1.0 and 0.5 there is a decrease in K concentration with increasing Cp/Ap ratio reflecting that the release of  $K^+$  from Cp extra-framework sites is driven by cation exchange with  $Ca^{2+}$  that is released by the dissolution of the synthetic Ap. The concentration of K as well as the decrease in K concentration with increasing Cp/Ap ratio (e.g. slope of the  $[K]$  vs. Cp/Ap ratio line in Fig. 5) is greater for  $E_K = 1$  in comparison to  $E_K = 0.5$  reflecting that K is the only exchangeable cation present on extra-framework sites of the Cp for the  $E_K = 1$  samples. Potassium concentrations from K-exchanged Cp and NCPR samples reported by Allen et al. [5] are shown in Fig. 5 and for a given Cp/Ap ratio are lower than the K concentrations for the  $E_K = 1$  samples reported here.

### 3.1.5. Ammonium

Solution  $NH_4^+$  concentrations as a function of Cp/Ap ratio and  $E_K$  are shown in Fig. 6 and show trends similar to K. The concentration of  $NH_4^+$  as well as the decrease in  $NH_4^+$  concentration with increasing Cp/Ap ratio (e.g. slope of the  $[NH_4^+]$  vs. Cp/Ap ratio line in Fig. 6) is greater for  $E_K = 0$  in comparison to  $E_K = 0.5$  reflecting that  $NH_4^+$  is the dominant exchangeable cation present on Cp extra-framework sites for the  $E_K = 0$  samples.

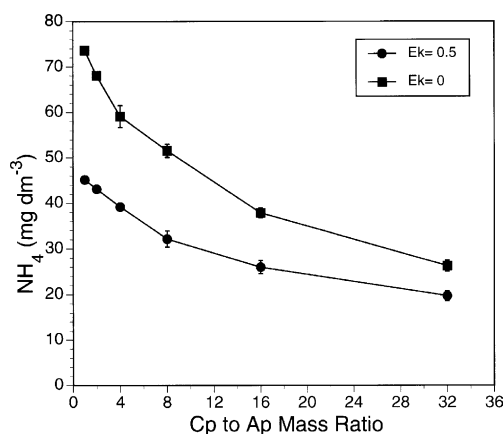


Fig. 6. Solution ammonium concentration as a function of Cp to Ap mass ratio and  $E_K$ . Symbols represent the average of three replicates. Error bars represent  $\pm 1\sigma$ . Lines connecting data points are added to show trends only and do not imply curve fitting.

### 3.2. Addition of Cal, Dol or Wol

The measured solution pH, ionic strength, and phosphorus, ammonium, potassium, magnesium and calcium concentrations after 500 h of shaking time for samples containing various amounts of Cal, Dol or Wol are shown in Table 5. The pH ranged from 8.0 to 8.5 and varied systematically with the amount added Cal, Dol or Wol. A control sample containing no additional Ca-bearing mineral had a pH of 8.0. Addition of Cal, Dol or Wol systematically raised the pH to 8.5, 8.2 or 8.4, respectively.

#### 3.2.1. Phosphorus

Phosphorus in solution is a result of the dissolution of Ap. The addition of Cal, Dol or Wol should inhibit the dissolution of Ap and result in lower solution P concentrations due to the common ion effect. The measured solution P concentration as a function of wt.% of added Cal, Dol or Wol is listed in Table 5 and shown graphically in Fig. 7. P concentration in solution decreases systematically with added Cal, Dol and Wol from a maximum of  $15.05 \text{ mg dm}^{-3}$  with no added mineral to a minimum of  $1.49 \text{ mg dm}^{-3}$  for 50 wt.% added Cal. The reduction in P represents reduced dissolution of Ap due to the common ion effect of additional Ca in solution. For each wt.% studied the addition of Cal resulted in the largest reduction of P concentration. The addition of Dol had the least effect and Wol had an intermediate effect. This relationship is consistent with the solubilities of Cal, Dol and Wol (Table 1). A linear least squares regression of the P concentration in solution data indicates that the relationship between P concentration in solution and wt.% of added Cal, Dol or Wol can be best correlated by an exponential function (Fig. 7) of the form:

$$[P] = [P_0] * e^{-kx}$$

$[P]$  = P concentration in solution;  $[P_0]$  = P concentration in solution ( $15.045 \text{ mg dm}^{-3}$ ) with 0.0 wt.% of added Cal, Dol or Wol;  $k$  = rate of decrease ( $\text{wt.}\%^{-1}$ );  $x$  = wt.% of added Cal, Dol or Wol (in decimal form).

The values of  $k$  are  $5.60 \text{ wt.}\%^{-1}$  for Cal ( $R^2 = 0.991$ ),  $2.85 \text{ wt.}\%^{-1}$  for Wol ( $R^2 = 0.995$ ), and

Table 5

pH, Ionic strength (IS), and concentrations of phosphorus, calcium, magnesium, potassium and ammonium as a function of wt.% calcite, dolomite or wollastonite

Cal (wt.%)	Dol (wt.%)	Wol (wt.%)	pH	IS (mmol dm <sup>-3</sup> )	P (mg dm <sup>-3</sup> )	Ca (mg dm <sup>-3</sup> )	Mg (mg dm <sup>-3</sup> )	K (mg dm <sup>-3</sup> )	NH <sub>4</sub> (mg dm <sup>-3</sup> )
0	0	0	8.0 (0.01)	3.91 (0.01)	15.05 (0.19)	0.51 (0.04)	1.33 (0.01)	23.6 (0.53)	36.3 (0.23)
5			8.2 (0.01)	3.92 (0.02)	10.24 (0.59)	0.65 (0.06)	1.31 (0.09)	25.3 (0.40)	37.3 (0.26)
10			8.2 (0.04)	3.97 (0.04)	8.48 (0.41)	0.82 (0.11)	1.34 (0.08)	25.9 (1.55)	38.6 (0.18)
15			8.3 (0.04)	3.96 (0.10)	6.73 (0.87)	0.93 (0.13)	1.41 (0.14)	24.5 (1.05)	37.9 (1.78)
20			8.3 (0.08)	4.00 (0.07)	5.00 (0.44)	1.16 (0.05)	1.47 (0.03)	25.6 (1.34)	38.5 (0.48)
25			8.4 (0.01)	4.06 (0.06)	3.89 (0.35)	1.32 (0.02)	1.54 (0.04)	26.7 (1.32)	39.4 (0.91)
50			8.5 (0.01)	3.75 (0.02)	1.49 (0.09)	2.47 (0.09)	1.56 (0.03)	26.1 (0.94)	36.5 (0.48)
	5		8.0 (0.00)	3.98 (0.08)	13.93 (0.21)	0.53 (0.08)	1.48 (0.09)	25.8 (0.25)	38.7 (0.40)
	10		8.0 (0.02)	3.83 (0.07)	12.44 (0.66)	0.59 (0.06)	1.51 (0.14)	25.6 (0.66)	37.5 (0.90)
	15		8.1 (0.02)	3.84 (0.03)	11.96 (0.26)	0.62 (0.03)	1.61 (0.05)	24.8 (0.42)	38.2 (0.49)
	20		8.1 (0.02)	3.75 (0.08)	11.53 (0.28)	0.65 (0.04)	1.64 (0.02)	24.0 (0.68)	37.9 (0.38)
	25		8.2 (0.03)	3.69 (0.05)	9.87 (0.26)	0.68 (0.03)	1.75 (0.09)	24.8 (1.14)	37.5 (0.23)
	50		8.2 (0.04)	3.31 (0.03)	6.72 (0.29)	0.79 (0.03)	2.11 (0.10)	23.1 (0.15)	33.3 (0.00)
		5	8.1 (0.03)	3.98 (0.13)	13.01 (0.77)	0.73 (0.09)	1.27 (0.17)	25.4 (0.84)	39.2 (1.01)
		10	8.1 (0.02)	3.99 (0.04)	11.14 (0.27)	0.89 (0.01)	1.35 (0.04)	25.9 (0.39)	39.0 (0.15)
		15	8.2 (0.04)	3.80 (0.03)	9.42 (0.53)	0.93 (0.02)	1.30 (0.01)	25.4 (0.74)	39.6 (0.92)
		20	8.3 (0.01)	3.67 (0.04)	8.37 (0.53)	0.96 (0.14)	1.18 (0.05)	24.5 (1.03)	39.8 (0.72)
		25	8.3 (0.02)	3.69 (0.04)	7.36 (0.21)	1.10 (0.09)	1.24 (0.08)	24.6 (1.32)	39.0 (1.02)
		50	8.4 (0.01)	3.36 (0.06)	4.22 (0.08)	1.68 (0.18)	1.14 (0.03)	24.0 (0.96)	35.4 (0.51)

Values represent average of three replicates. Numbers in parentheses represent one standard deviation.

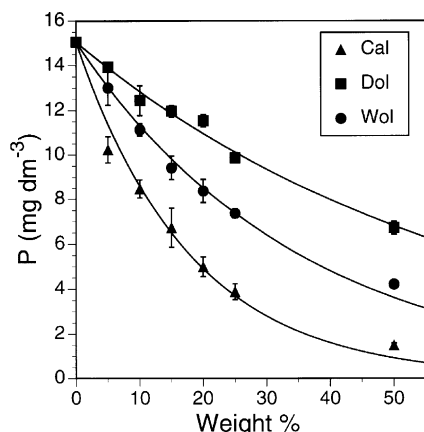


Fig. 7. Solution phosphorus concentration as a function of weight percent of added calcite (Cal), dolomite (Dol) or wollastonite (Wol). Error bars represent  $\pm 1\sigma$ . Derived curves are of the form  $[P] = [P_0] * e^{-kx}$  where the values of  $k$  are 5.60 for Cal ( $R^2 = 0.991$ ), 2.85 for Wol ( $R^2 = 0.995$ ), and 1.58 for Dol ( $R^2 = 0.987$ ).

1.58 wt.%<sup>-1</sup> for Dol ( $R^2 = 0.987$ ). The order of the  $k$  values (Cal > Wol > Dol) can be correlated with the solubility products for these three minerals (see below).

### 3.2.2. Calcium

Equilibrium  $Ca^{2+}$  concentrations in solution will be the result of the dissolution of Ap and Cal, Dol or Wol and of the cation exchange of  $Ca^{2+}$  with  $K^+$  and  $NH_4^+$  on extra-framework sites in Cp. Because Cal, Dol and Wol are all much more soluble than Ap, their addition to the Ap plus Cp mixture should result in higher concentrations of  $Ca^{2+}$  in solution. Calcium concentrations in solution as a function of wt.% of added Cal, Dol or Wol are shown in Fig. 8. Calcium concentrations in solution increase systematically from a value of 0.51 mg dm<sup>-3</sup> for the Ap only system after added Cal, Dol and Wol. Similar to the P data, Cal has the greatest effect and Dol the least effect on the change in  $Ca^{2+}$  concentration in solution and is consistent with the solubilities of Cal, Dol and Wol (Table 1). A linear least squares regression of the  $Ca^{2+}$  concentration in solution data indicates that the relationship between  $Ca^{2+}$  concentration in solution and wt.% of added Cal, Dol or Wol can be correlated by a linear function (Fig. 8) of the form:

$$[Ca] = mx + [Ca_0]$$

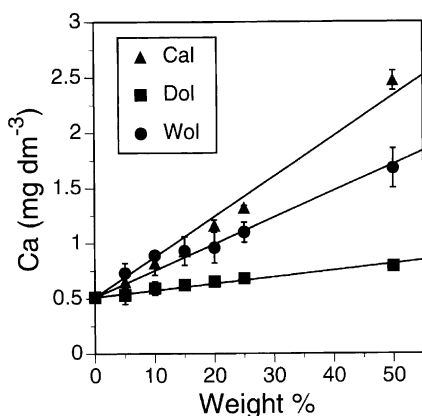


Fig. 8. Solution calcium concentration as a function of weight percent calcite (Cal), dolomite (Dol) or wollastonite (Wol). Error bars represent  $\pm 1\sigma$ . Derived curves are of the form  $[Ca] = mx + [Ca_0]$  where the values of  $m$  are 3.64 for Cal ( $R^2 = 0.984$ ), 2.41 for Wol ( $R^2 = 0.967$ ), and 0.61 for Dol ( $R^2 = 0.967$ ).

$[Ca] = Ca^{2+}$  concentration in solution;  $[Ca_0] = Ca^{2+}$  concentration in solution ( $0.51 \text{ mg dm}^{-3}$ ) with 0.0 wt.% of added Cal, Dol or Wol;  $m = \text{rate of increase (mg dm}^{-3} \text{ wt.\%}^{-1})$ ;  $x = \text{wt.\% of added Cal, Dol or Wol (in decimal form)}$ .

The values of  $m$  are  $3.64 \text{ mg dm}^{-3} \text{ wt.\%}^{-1}$  for Cal ( $R^2 = 0.984$ ),  $2.41 \text{ mg dm}^{-3} \text{ wt.\%}^{-1}$  for Wol ( $R^2 = 0.967$ ), and  $0.61 \text{ mg dm}^{-3} \text{ wt.\%}^{-1}$  for Dol ( $R^2 = 0.967$ ). The order of the  $m$  values (Cal > Wol > Dol) can be correlated with the solubility products for these three minerals (see below).

### 3.2.3. Magnesium

Magnesium in solution is a result of the dissolution of Ap which contains 2.25 wt.% MgO (Table 2) and, when present, the dissolution of Dol which contains 17.66 wt.% MgO (Table 3). Cation exchange of  $Mg^{2+}$  with  $K^+$  and  $NH_4^+$  in the Cp would be expected to be minimal due to the high selectivity of  $K^+$  and  $NH_4^+$  over  $Mg^{2+}$  in Cp. According to Ames [43] the ion selectivity order for Cp cations is  $Cs^+ > Rb^+ > K^+ > NH_4^+ > Ba^{2+} > Sr^{2+} > Na^+ > Ca^{2+} > Fe^{3+} > Al^{3+} > Mg^{2+} > Li^+$ . However, data from the present study (see Fig. 4) suggest that some cation exchange of  $Mg^{2+}$  with  $NH_4^+$  does occur. The addition of Cal or Wol to the Cp and Ap mixture should result in reduced dissolution of Ap due to the common ion effect and consequently

reduced solution Mg concentrations. The overall effect of adding Dol on solution Mg concentrations will be the sum of two competing effects: (1) reduced Ap dissolution due to the common ion effect and (2) Mg released into solution from the dissolution of Dol. Krauskopf and Bird [27] point out that the presence of ions in solution (e.g.,  $Mg^{2+}$ ) not present in a salt (e.g., Ap), will tend to make the salt more soluble. In this case the salt in question, Ap, does contain a small amount (2.25 wt.% MgO) of Mg and it is unclear if the  $Mg^{2+}$  in solution due to Dol dissolution will have any effect on Ap dissolution that will be discernable from the common ion effect due to Ca.

The measured solution Mg concentration as a function of wt.% of added Cal, Dol or Wol is listed in Table 5 and shown graphically in Fig. 9. Magnesium concentrations in solution increase systematically with added Dol from a value of  $1.33 \text{ mg dm}^{-3}$  for the Ap only system. A linear least squares regression of the Mg concentration in solution data indicates that the relationship between Mg concentration in solution and wt.% added Dol can be correlated by a linear function (Fig. 9) of the form:

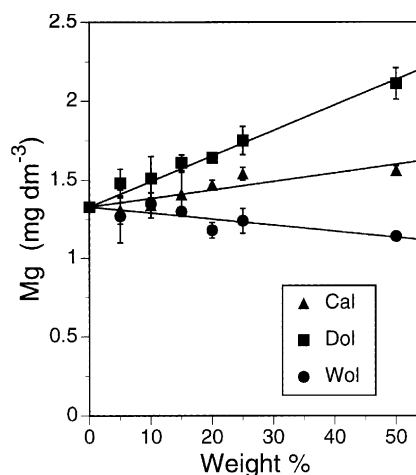


Fig. 9. Solution magnesium concentration as a function of weight percent calcite (Cal), dolomite (Dol) or wollastonite (Wol). Error bars represent  $\pm 1\sigma$ . Derived curves are of the form  $[Mg] = mx + [Mg_0]$  where the values of  $m$  are 0.535 for Cal ( $R^2 = 0.805$ ),  $-0.394$  for Wol ( $R^2 = 0.688$ ), and 1.61 for Dol ( $R^2 = 0.985$ ).

$$[\text{Mg}] = mx + [\text{Mg}_0]$$

$[\text{Mg}]$  = Mg concentration in solution;  $[\text{Mg}_0]$  = Mg concentration in solution ( $1.33 \text{ mg dm}^{-3}$ ) with 0.0 wt.% of added Cal, Dol or Wol;  $m$  = rate of increase ( $\text{mg dm}^{-3} \text{ wt.}\%^{-1}$ );  $x$  = wt.% of added Dol (in decimal form).

The value of  $m$  is  $1.61 \text{ mg dm}^{-3} \text{ wt.}\%^{-1}$  for Dol ( $R^2 = 0.985$ ). Both Cal and Wol do not show a strong correlation between Mg concentration in solution and wt.% added Cal or Wol. There is a weak negative correlation with wt.% added Wol ( $m = -0.394 \text{ mg dm}^{-3} \text{ wt.}\%^{-1}$ ,  $R^2 = 0.688$ ) that can be explained by reduced Ap dissolution due to the common ion effect. There is a weak positive correlation between Mg concentration in solution and wt.% added Cal ( $m = 0.535 \text{ mg dm}^{-3} \text{ wt.}\%^{-1}$ ,  $R^2 = 0.805$ ).

### 3.2.4. Potassium

Potassium in solution is a result of cation exchange between  $\text{K}^+$  on extra-framework exchange sites in the Cp and  $\text{Ca}^{2+}$  in solution. Because the origin of the  $\text{Ca}^{2+}$  in solution (dissolution of Ap vs. dissolution of Cal, Dol or Wol) is inconsequential on cation exchange equilibria there should be no net effect on solution  $\text{K}^+$  concentrations due to the addition of Cal, Dol or Wol. A possible exception could occur if the total sample contained only a small amount of Cp. Potassium concentrations in solution as a function of wt.% of added Cal, Dol or Wol are shown in Fig. 10. By taking into account the standard deviations, K concentration in solution does not change with wt.% added Cal, Dol or Wol, except for a small decrease for the mixture with 50 wt.% Dol.

### 3.2.5. Ammonium

The effect on solution  $\text{NH}_4^+$  concentrations with the addition of Cal, Dol or Wol should be similar to the effect expected for  $\text{K}^+$ . Ammonium concentrations in solution as a function of wt.% of added Cal, Dol or Wol are shown in Fig. 11. With the exception of the 50 wt.% samples,  $\text{NH}_4^+$  concentration in solution does not change with wt.% added Cal, Dol or Wol.

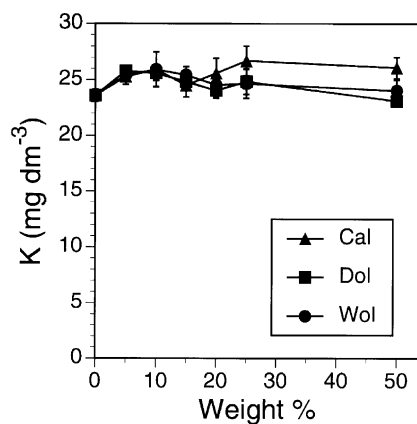


Fig. 10. Solution potassium concentration as a function of weight percent calcite (Cal), dolomite (Dol) or wollastonite (Wol). Error bars represent  $\pm 1\sigma$ .

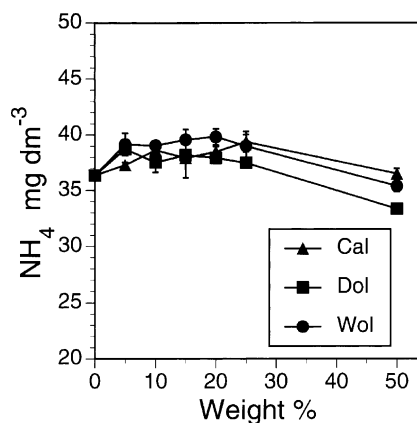


Fig. 11. Solution ammonium concentration as a function of weight percent calcite (Cal), dolomite (Dol) or wollastonite (Wol). Error bars represent  $\pm 1\sigma$ .

## 4. Discussion

### 4.1. The common ion effect

The addition of Cal, Dol and Wol to mixtures of Cp and Ap changes the concentrations of P and  $\text{Ca}^{2+}$  in solution in a continuous and systematic fashion that is consistent with changes expected due to the common ion effect. The response of P and  $\text{Ca}^{2+}$  in solution to the addition of Cal, Dol or Wol is greatest for Cal, intermediate for Wol and the least for Dol. This response can be correlated

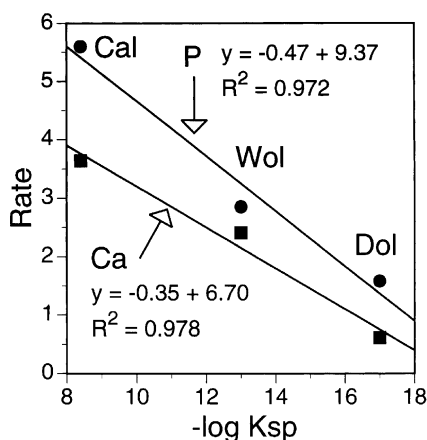


Fig. 12. Rate coefficients with additional calcite (Cal), wollastonite (Wol) or dolomite (Dol), (rate of decrease for P (from Fig. 7), rate of increase for Ca (from Fig. 8)) versus the solubility products of calcite ( $-\log K_{sp} = 8.4$ , midpoint of range in [23]), wollastonite ( $-\log K_{sp} = 13$ , from [21]), and dolomite ( $-\log K_{sp} = 17$ , from [21]).

with the solubilities of these minerals. Plotted in Fig. 12 are the rate coefficients (described above) for P and Ca with additional Cal, Wol or Dol ( $k$  = rate of decrease for P,  $m$  = rate of increase for Ca) versus the solubility products for these minerals from Table 1. There is a linear correlation between the rate coefficient and solubility product. Both P and Ca have a linear least squares correlation coefficient ( $r^2$ ) greater than 0.97. Albeit the correlation is based on only three data points, those three data points represent a reduction of data from 57 experiments.

The decrease in dissolution of Ap, as reflected by the decrease in P concentration, with addition of Cal, Dol and Wol cannot be attributed solely to pH. The variation in pH in all the samples studied is from 8 to 8.5 (Table 5). Using the chemical equilibrium speciation program Visual Minteq, the expected range of total P in solution in equilibrium with Ap and atmospheric  $\text{CO}_2$  is from 0.33 (pH = 8) to 0.19 (pH = 8.5)  $\text{mg dm}^{-3}$ . The variation in P concentration as a function of pH observed in the present study is an order of magnitude greater than predicted by Visual Minteq (Fig. 13a). The trend in Ca concentrations in solution observed in the present study is opposite to the trend expected due to a change in pH (Fig.

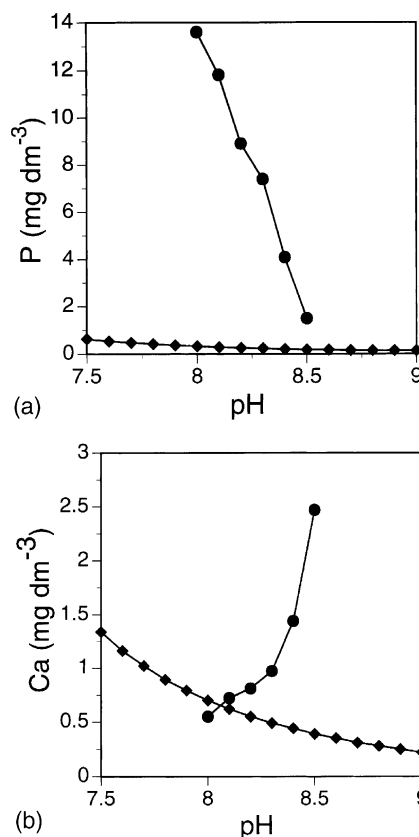


Fig. 13. Variation in phosphorus (13a) and calcium (13b) concentrations observed in the present study (circles) as a function of pH compared with values predicted by Visual Minteq (diamonds) for a solution in equilibrium with Ap and atmospheric  $\text{CO}_2$ .

13b). Average Ca in solution data for pH 8 in the present study is  $0.5 \text{ mg dm}^{-3}$  increasing to a value of  $2.5 \text{ mg dm}^{-3}$  for pH 8.5. Total Ca in solution predicted by Visual Minteq for this same pH region decreases from  $0.7 \text{ mg dm}^{-3}$  (pH = 8) to  $0.4 \text{ mg dm}^{-3}$  (pH = 8.5).

#### 4.2. Inferences on nutrient availability

Schofield [44] addresses nutrient availability in soils by distinguishing between nutrient intensity (i.e. represented by the concentration of the soil solution) and nutrient quantity or capacity (i.e. the amount of potentially available nutrient in the soil). The results of the present study can be used to assess only the initial nutrient intensity. Kinetic

Table 6

Nutrient concentration ( $\text{mg dm}^{-3}$ ) from the present studied compared with various soil solutions

	P	Ca	Mg	Ammonium-N	Total N	K	Reference
The present study	0.57–15.05	0.47–3.40	0.11–6.68	19.7–73.6	19.7–73.6	14.8–104.8	
Hoagland's nutrient solution		200					[45]
Average soil solution		339.5					[46]
Hydroponic system just adequate		0.24–40					[47]
Soil solution	0.19–0.31	8.02–44.9				9–60	[48]
Hydroponic solution at a lunar outpost	31	50	16		202	156	[49]
Annual average soil solution for arable soils	0.14	66.1	11.9	0.9	193	19.9	[50,51]
Soil solution	0.003–0.3		5–50			1–10	[52]

studies, plant growth studies, and/or special soil tests are required to address nutrient quantity.

Concentrations of the soil nutrients phosphorus, calcium, magnesium, ammonium-N and potassium measured in the present study are compared in Table 6 with concentrations for soil and hydroponic solutions. Phosphorus concentrations are greater than soil solution concentrations but are lower than Bugbee and Salisbury's [49] estimated ideal P concentration for a hydroponic system at a Lunar outpost. Calcium concentrations are low compared to soil solutions and hydroponic solutions including the half strength Hoagland's nutrient solution [45] used as a control in NASA's zeoponic plant growth experiments [13,15,16]. Except for two-mineral treatments with a Cp/Ap ratio of 1 and an  $E_K$  of 1 or 0.5, Mg concentrations are low compared to soil and hydroponic solutions. Ammonium-N concentrations are far above-recommended soil solution  $\text{NH}_4^+$  concentrations, however, total N concentrations are low compared to soil and hydroponic solutions. Potassium concentrations are greater than or comparable to the range of reported soil solutions but are lower than the recommended concentration for a hydroponic system at a Lunar outpost.

#### 4.3. Removal of P by Wol

Henderson et al. [16] and Steinberg et al. [15] included ferrihydrite in their zeoponic substrates to sequester P. In a study of P removal by Wol (using Wol mined from the same locality as the present study) Brooks et al. [53] reported reduced

levels of P in solution over time when 5 and 10  $\text{mg dm}^{-3}$  phosphate solutions were exposed to Wol using a 20:1 solution to Wol ratio (40 ml phosphate solution to 2 g of pure Wol) and attributed the mechanism to either adsorption of P on the Wol surfaces or precipitation of calcium phosphates. The reduced P concentrations in solution with the addition of Cal, Dol and Wol reported in the present study are not consistent with either mechanism proposed by Brooks et al. [53] because an adsorption of P on the Wol (or Cal or Dol) surfaces would not co-vary with the increase in  $\text{Ca}^{2+}$  concentrations in solution reported here. A reduction on P concentrations in solution due to the precipitation of calcium phosphates as proposed by Brooks et al. [53] would be expected to co-vary with reduced  $\text{Ca}^{2+}$  concentrations in solution, opposite to the trend reported in the present study.

## 5. Conclusions

Dissolution of synthetic Ap in the presence of Cp results in greater dissolution of the synthetic Ap because it is driven by ion exchange of  $\text{Ca}^{2+}$  onto extra-framework sites in the Cp, releasing  $\text{K}^+$  and/or  $\text{NH}_4^+$  into solution. The specific amounts of these macronutrients in solution, as well as calcium, are a function of the Cp/Ap ratio in the sample and to the ratio of  $\text{K}^+$  and/or  $\text{NH}_4^+$  on the extra-framework sites in Cp. Solution concentrations of ammonium, potassium, calcium and magnesium all decrease with increasing Cp/Ap ratio in the sample. Potassium and  $\text{NH}_4^+$  exhibit

similar trends due to the fact that both ions originate on Cp extra-framework sites and undergo cationic exchange with  $\text{Ca}^{2+}$  and other ions. Calcium and magnesium show similar trends due to their common origin in the synthetic Ap crystalline structure. Solution concentrations of phosphorus initially increased until a maximum value was reached and then decreased with increasing Cp/Ap ratio in the sample for these experiments. The Cp/Ap ratio at which the maximum solution concentration of phosphorus occurs varies as a function of  $E_K$  of the Cp. The observed trends, using synthetic Ap, in solution phosphorus concentrations as a function of Cp/Ap ratios are comparable with data reported for naturally occurring Ap in combined PR and Cp systems [5,9–11]. The macronutrients phosphorus, ammonium-N, and potassium are available to plants at sufficient levels. Magnesium concentrations are marginal. Concentrations of  $\text{Ca}^{2+}$  in solution may be insufficient for plant growth. Calcium is exchanged onto the extra-framework sites of Cp, which reduces its concentration in solution. Plant growth studies using zeoponic substrates have resulted in poor seed production in wheat, which has been attributed to Calcium deficiency and/or high phosphorus concentrations [13,15]. The addition of Cal, Dol or Wol to a zeoponic substrate results in increased  $\text{Ca}^{2+}$  and reduced phosphorus in solution. The addition of a second Ca-bearing mineral is a viable remedy to the problem of poor seed production in wheat (see Gruener et al. this issue). Zeoponic substrates containing Cal, Dol or Wol can provide essential plant nutrients and a solid support substrate for plant growth during long duration space missions.

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